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Structure Properties of As-synthesized Cu-doped ZnO Nanopowder Synthesized by Co-precipitation Method

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Abstract

pure ZnO and Cu - doped ZnO nanopowders (1, 2, 3, 4 and 5 wt% Cu) were synthesized by co-precipitation method without further post-heat treatment. The as-synthesized powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and Raman spectroscopy. The XRD results represented as-synthesized Cu-doped ZnO nanopowders in hexagonal wurtzite structure and SEM images demonstrated the shape and size of as-prepared samples. In addition, Raman spectra confirm space group of ZnO. All results indicated significant influence of Cu doping on relevant structural properties of ZnO.

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Keywords : Cu-doped ZnO nanopowder ; Co-precipitation method.

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1. Introduction

ZnO is an n-type semiconductor with wide energy band gap of 3.37 eV and high exciton binding energy of 60 meV. ZnO oxide is one of most-widely used and versatile metal oxide semiconductor materials because of its fascinating optical, chemical, physical, and electrical properties. Due to these properties, ZnO is recognized as highly potential candidate for electronic and optoelectronic applications. Meanwhile, there have been several reports focused on the effort to adjust the properties of ZnO by doping with transition metal such as Al [1], Co [2], Ni [3] ,Cu [4-5]. Among promising dopants, Cu is known as preferable dopant due to its advanced attributes such as low toxicity and source abundance. Recently, Cu-doped ZnO has shown singnificant improvement in relevant properties such as electrical, magnetic, photocatalytic performance and gas sensing [4-7].

In this work, The syntheses of Cu-doped ZnO nanopowders using co-precipitation method using zinc nitrate ($Zn(NO_3)_2.6H_2O$), copper(II) nitrate trihydrate ($Cu(NO_3)_2.3\ H_2O$) and sodium hydroxide as starting precursors. The properties of as-synthesized Cu-doped ZnO nanopowders were throughly investigated by XRD, SEM and Raman spectroscopy.

2. Experimental

Nanopowders of Cu-doped ZnO with 0, 1, 2, 3, 4 and 5 wt% Cu, have been synthesized via co-precipitation method using zinc nitrate ($Zn(NO_3)_2.6H_2O$), copper(II) nitrate trihydrate ($Cu(NO_3)_2.3\ H_2O$) and sodium hydroxide (NaOH) as starting materials. For preparation of Cu-doped ZnO nanopowder , 0.5 M of zinc nitrate was dissolved in 100 ml deionized water and certain amount copper (II) nitrate trihydrate was added according to doping condition in solution. NaOH solution was slowly added into the precursor under vigorous stirring until pH of the solution reached to 14, leading to the precipitated product. After that, as-precipitated products were washed several times with dionized water and ethanol in the last step until they became neutral. Finally, the products were dried in oven at 80ºC for 6 h.

3. Result and Discussion

Figure 1 shows typical XRD patterns of the as-synthesized undoped and Cu-doped ZnO with varying concentration of copper. The peak positions of all samples correspond to ZnO according to the standard JCPDS card and is indexed as the hexagonal wurtzite. As seen in XRD patterns, the appearance of additional CuO peak is observed in the doped samples with 4% and 5% Cu doping content.The peak are negligibly very small, indicating ignorable change in ZnO crystal structure with Cu additive and the mixture phase of ZnO and CuO at high Cu doping content.

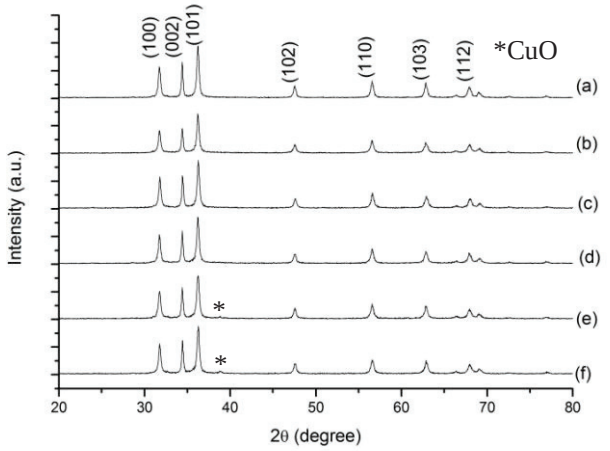

Fig. 1. X-ray diffraction patterns of as-synthesized ZnO nanopowder doped with (a) 0 wt% Cu, (b) 1 wt% Cu, (c) 2 wt% Cu, (d) 3 wt% Cu, (e) 4 wt% Cu, (f) 5 wt% Cu

Based on XRD results, the average crystallite size (D) can be calculated from the most intense diffraction peak (101) using well-known Debye-Scherrer's equation;

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{1}$$

where D is the average crystallite size, κ is the shape factor , λ is the wavelength of incident x-ray beam , β is the full - width at the half maximum (FWHM) in radius on 2θ scale and θ is the Bragg's diffraction angle . The average crystallite sizes was found to be about 25-27 nm. The lattice constant for hexagonal wurtzite ZnO nanopowders are estimated from equation ;

$$\frac{1}{d^2} = \frac{4}{3\left(h^2 + hk + k^2/a^2\right)} + \frac{l^2}{c^2} \tag{2}$$

where a and b are the lattice constant, h, k and l are the miller indices and d is the interplanar spacing. Note that, the interplanar spacing can be calculated from Bragg's low ;

$$2d\sin\theta = \mathrm{n}\lambda \tag{3}$$

In addition, the micro-strain(ε) of samples are calculated by the following equation ;

$$\text{Micro-strain}\,(\varepsilon) = \frac{\beta\cos\theta}{4} \tag{4}$$

where ε is The micro-strain, β is the full – width at the half maximum (FWHM) in radius on 2θ scale and θ is the Bragg's diffraction angle. The micro-strain are found to be 0.0126-0.3145. The crystalline size, lattice parameter and the micro - strain are presented in Table 1. Figure 2 illustrates the morphologies of the as-synthesized undoped and Cu-doped ZnO nanopowders (a) 0 wt%, (b) 1 wt% , (c) 2 wt% Cu, (d) 3 wt%, (e) 4 wt% , (f) 5 wt% respectively were examined with SEM. The typical morphologies of sample in all concentration of Cu-doped are found to be in cluster form of hierarchical structure with sharp tip or needle-like structure. The average size of the particles monitored by SEM is less than 100 nm, that is in good accordance with XRD result. All SEM results suggest that shape and size of ZnO nanostructures prepared by co-precipitation method highly depend on Cu additive.

Fig. 3 displays the Raman spectra of as-synthesized ZnO. The significant peak of the E_2 (High) mode at 436 cm^{-1} represents Wurtzite hexagonal structure of ZnO. Another observable spectra positioned at 330, 380, 578 cm^{-1} are attributable to E_{2H}-E_{2L}, A_1(TO) and A_1(LO) modes, respectively. Figure 4. Shows Raman shift of as-synthesized Cu - doped ZnO nanopowder with varying concentration of copper. For all doped samples, the main peak of the E_2 (High) mode at around 427 cm^{-1} and another spectra positioned at 318, 561 cm^{-1} are attributable to E_{2H}-E_{2L} and A_1(LO) modes, respectively. It is observed as the Cu doping concentration increases, intensities of spectra decrease and the A_1(TO) mode was vanished, suggesting the deterioration of ZnO bonding changing upon the Cu doping. Note that, TO is transverse optical phonon and LO is longitudinal optical phonon. A_1 and E_1 modes are polar phonon mode and split into TO and LO and both A_1 and E_1 modes are Raman and IR active modes. The E_2 mode is a non-polar phonon and active with Raman only, meanwhile B_1 mode is Raman and IR inactive mode[8].

Table 1. The crystalline size, lattice parameter and the micro – strain of as-synthesized Cu – doped ZnO nanopowder

Copper content (wt%)	Crystalline size(nm)	Lattice constant		Micro-strain
		a=b (Å)	c (Å)	
0	27.8096	2.8136	5.2040	0.00126
1	24.8495	2.8131	5.2042	0.00133
2	25.5704	2.8096	5.1972	0.00134
3	25.8490	2.8137	5.2039	0.00133
4	25.4491	2.8128	5.2030	0.00145
5	25.7474	2.8111	5.1991	0.00137

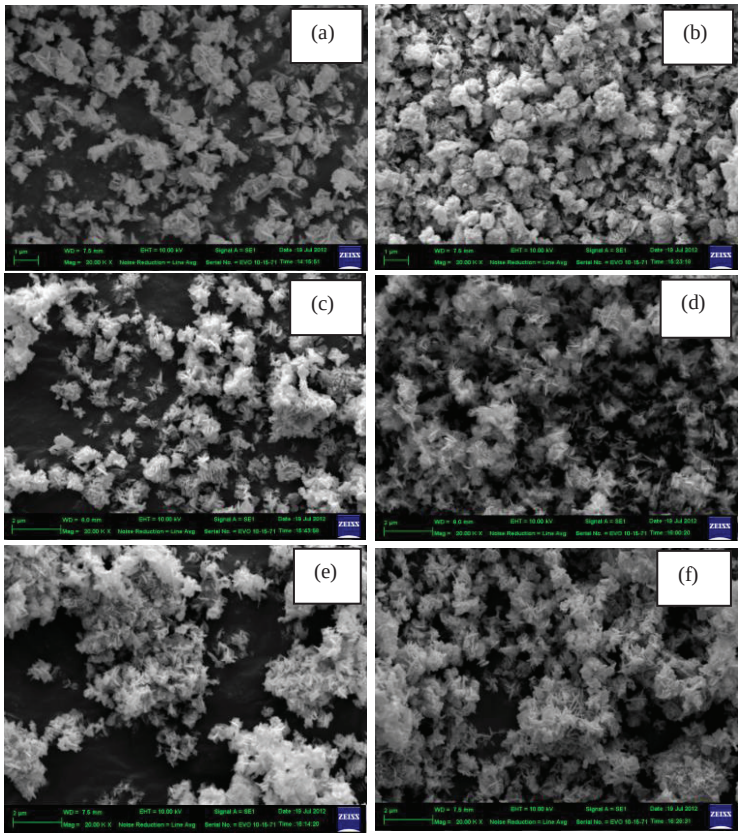

Fig. 2. SEM images of the as-synthesized ZnO nanopowder doped with (a) 0 wt% Cu, (b) 1 wt% Cu, (c) 2 wt% Cu, (d) 3 wt% Cu, (e) 4 wt% Cu, (f) 5 wt% Cu

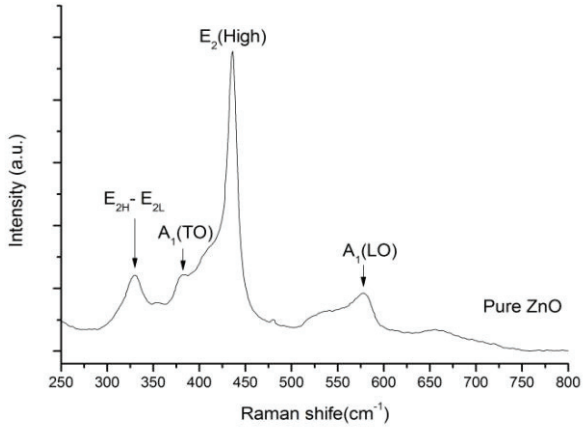

Fig. 3. Room-temperature Raman shift of as-synthesize ZnO nanopowder

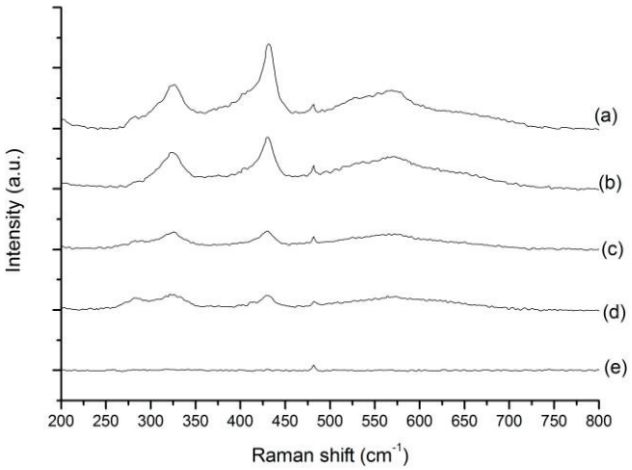

Fig. 4 Raman shift of as-synthesize Cu - doped ZnO nanopowder with (a) 1 wt% , (b) 2 wt%, (c) 3 wt% , (d) 4 wt% , (e) 5 wt%

4. Conclusion

In summary, the as-synthesized ZnO and Cu-doped ZnO nanopowders have been successfully prepared using co-precipitation method. The XRD results confirmed that the crystal structure of all as-synthesized samples is hexagonal wurtzite with average crystallite sizes is approximately 25-27 nm corresponding to interplanar spacing, lattice constant and micro-strain of as-synthesized powders. The SEM results indicate that the shape and size of nanostructure. Raman peaks shift to lower frequencies due to increase Cu doping content.

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